DETECTION OF INTRAMOLECULAR CHARGE TRANSFER AND DYNAMIC SOLVATION IN EOSIN B BY FEMTOSECOND TWO-DIMENSIONAL ELECTRONIC SPECTROSCOPY

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We have employed 2D electronic photon echo spectroscopy to study intramolecular charge-transfer dynamics in eosin B. After preparation of the first excited singlet state (S_1) with 40-fs excitation pulses at 520 nm, the nitro group (–NO_2) in eosin B undergoes excited state torsional motion towards a twisted intramolecular charge transfer (TICT) state. As the viscosity of the surrounding solvent increases, the charge-transfer rate decreases because the twisting of the –NO_2 group is hindered. These conclusions are supported by the time evolution of the 2D spectrum, which provides a direct measure of the the ground-to-excited-state energy gap time-correlation function, $M(t)$. In comparison to the inertial and diffusive solvation time scales exhibited by eosin Y, which lacks the nitro group, the $M(t)$ function for eosin B exhibits under the same conditions an additional component on the 150-fs timescale that arises from quenching of the S_1 state by crossing to the TICT state. These results indicate that 2D electronic spectroscopy can be used as a sensitive probe of the rate of charge transfer in a molecular system and of the coupling to the motions of the surrounding solvent. (Supported by grant DE-SC0010847 from the Department of Energy, Office of Basic Energy Sciences, Photosynthetic Systems program.)